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# Linear aspects of the Korringa–Kohn–Rostoker formalism

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## Abstract

We present the one-dimensional Korringa–Kohn–Rostoker (KKR) method with the aim of elucidating its linear features, particularly important in optimizing the numerical algorithms in energy band computations. The conventional KKR equations based on multiple scattering theory as well as novel forms of the secular matrix with nearly linear energy dependency of the eigenvalues are presented. The quasi-linear behaviour of these eigenvalue functions appears after (i) re-normalizing the wavefunctions in such a way that ‘irregular’ solutions vanish on the boundary of the ‘muffin-tin’ segments, and (ii) integrating the full Green function over the whole Wigner–Seitz cell. In addition, using the aforementioned approach we derive a one-dimensional analogue of the generalized Lloyd formula.

The novel KKR approach illustrated in one dimension can be almost directly applied to higher dimensional cases. This should open prospects for the accurate KKR band structure computations of very complex materials.

## 1. Introduction

In the Korringa–Kohn–Rostoker (KKR) method [1, 2] the main problem in performing electronic structure calculations is due to strongly nonlinear dependence of the KKR-matrix eigenvalues on energy for a fixed  $k$ -point. It is very difficult to find all the zeros of eigenvalue functions properly, when there is a large number of atoms in the unit cell. Hence the fast and accurate extraction of all zeros of eigenvalues still remains a challenge in the computation of complex materials.

Butler [3] and Schwitalla *et al* [4] formulated the KKR formalism for one spatial dimension, which is very similar to its three-dimensional counterpart. The one-dimensional case is computationally much simpler and allows one to formulate the substantial results in compact, analytical forms. Therefore, it is very attractive to investigate features of the KKR method along this line.

In this paper we use the Green function (GF) approach for solving the Schrödinger equation. As is already known, the one-dimensional (1D) KKR method gives exact solutions. This is due to the facts that (i) the unit cell can be entirely filled by the non-overlapping (touching each other) ‘muffin-tin’ segments, and (ii) the multipole expansion contains only two ‘spherical harmonics’ ( $l = 0$  and  $1$ ). Furthermore, the KKR structure constants in the 1D case can be obtained analytically, which markedly facilitates numerical calculations.

In the context of other linearization techniques used in popular methods such as LMTO or LAPW, we would like to point out that in the KKR formalism satisfying boundary conditions is guaranteed by the construction of a periodic Green function with the reference system usually chosen as empty space. Also, in the KKR formalism we do not need to specify an energy independent set of basis functions, which is the starting point for the LMTO or LAPW methods when constructing a Bloch wavefunction. Instead of building up the secular equation with a Hamiltonian and overlapping matrices, we focus on finding the secular matrix within the KKR formalism with eigenvalue energy dependence possibly linear in a wide energy intervals.

Our paper is organized as follows. In section 2 we recall after Butler [3] and Schwitalla *et al* [4] the standard 1D-KKR formalism. In this section we also discuss a few difficulties in determining the band structure in multi-atom systems [5] if using the standard approach. Section 3 presents the novel form of the KKR-matrix in terms of logarithmic derivatives as well as the advantages of this approach with respect to the standard KKR theory. Next, the generalized Lloyd formula [6, 7] is derived, which helps in the computation of the total number of states and placing the Fermi energy properly at an early stage of calculations in real materials. In section 5 we show illustrative results for an arbitrary chosen potential, which are followed by a summary and conclusions (section 6).

## 2. Standard KKR formalism in one dimension

We look for a solution of the 1D Schrödinger equation with Hamiltonian (atomic units are used, energy unit is 1 Ryd)

$$H = -\frac{d^2}{dx^2} + V(x). \quad (1)$$

The potential in (1) is assumed to be translationally invariant with the period of lattice constant  $a$ , so it can be written as

$$V(x) = \sum_{n=-\infty}^{+\infty} v(x - na). \quad (2)$$

We assume  $v(x)$  in (2) to vanish for  $|x|$  greater than some radius  $S$ , and that they do not overlap each other. This assumption has a form analogous to the non-overlapping ‘muffin-tin’ potential in three-dimensional (3D) KKR theory. We shall expand the potential  $v(x)$  in (2) and the wavefunctions around each center into symmetric and antisymmetric functions, analogous to the 3D expansion into the spherical harmonics. First, let us define 1D spherical coordinates centred at the  $n$ -point,

$$x = \hat{x}r + na, \quad x \in \left[ na - \frac{a}{2}, na + \frac{a}{2} \right], \quad (3)$$

with discrete directional coordinate,  $\hat{x} = \text{sgn}(x - na)$ , and radius  $r \in \left[ 0, \frac{a}{2} \right]$ . Then, with the definition of the 1D analogue of the spherical harmonics

$$Y_0(\hat{x}) = 1/\sqrt{2} \quad Y_1(\hat{x}) = \hat{x}/\sqrt{2}, \quad (4)$$

we decompose  $v(x)$  into ‘spherical’ and ‘aspherical’ parts:

$$v(x) = \frac{1}{2}[v(r) + v(-r)] + \frac{\hat{x}}{2}[v(r) - v(-r)] = v_0(r)Y_0(\hat{x}) + v_1(r)Y_1(\hat{x}), \quad (5)$$

where

$$v_0(r) \equiv [v(r) + v(-r)]/\sqrt{2} \quad v_1(r) \equiv [v(r) - v(-r)]/\sqrt{2}. \quad (6)$$

Similarly, we may write the 1D multipole series for the wavefunction

$$\psi(x) = \psi_0(r)Y_0(\hat{x}) + \psi_1(r)Y_1(\hat{x}) \quad (7)$$

(where  $\psi_l(r)$  are defined analogically to  $v_l(r)$ ) with the radial functions of the free Schrödinger equation given by the following regular

$$j_0(\sqrt{E}r) = \cos(\sqrt{E}r) \quad j_1(\sqrt{E}r) = \sin(\sqrt{E}r) \quad (8)$$

and ‘irregular’

$$n_0(\sqrt{E}r) = \sin(\sqrt{E}r) \quad n_1(\sqrt{E}r) = -\cos(\sqrt{E}r) \quad (9)$$

special solutions. Also analogues of the 3D spherical Hankel functions, usually defined as  $h_l(x) = j_l(x) + in_l(x)$ , exist:

$$h_0(\sqrt{E}r) = \exp(i\sqrt{E}r) \quad h_1(\sqrt{E}r) = -i \exp(i\sqrt{E}r). \quad (10)$$

The square root  $\sqrt{E}$  is taken on the complex energy plane with the branch cut along the positive real axis. To proceed further we follow the steps in the multiple scattering formalism [8, 9], leading to the following form of the Bloch–Fourier GF:

$$\langle x'|G(E, k)|x \rangle = - \sum_l J_l(E, x_>)Z_l(E, x_<) + \sum_{l,l'} Z_{l'}(E, x')[t^{-1}(E) - B(E, k)]_{l'l}^{-1} Z_l(E, x). \quad (11)$$

In (11),  $Z_l(E, x)$  and  $J_l(E, x)$  are the regular and irregular solutions of the Schrödinger equation with the radial parts given in the asymptotic region ( $r \geq S$ ) by

$$[Z(E, r)]_{l'l} = j_{l'}(\sqrt{E}r)[t^{-1}(E)]_{l'l} - \frac{i}{\sqrt{E}}h_l(\sqrt{E}r)\delta_{l'l} \quad (12)$$

$$[J(E, r)]_{l'l} = j_{l'}(\sqrt{E}r)\delta_{l'l}. \quad (13)$$

$B(E, k)$  is the matrix of KKR structure constants with explicit form generalized to the multi-atom case as given in the appendix. The matrix  $t(E)$  is a one-scatterer  $t$ -matrix and may be found from the wavefunctions

$$\psi_l(E, x) = \sum_{l'} Y_{l'}(\hat{x})[\psi(E, r)]_{l'l} \quad (14)$$

with radial solutions satisfying the following set of differential equations:

$$\frac{d^2}{dr^2}\psi(E, r) + [E - v(r)]\psi(E, r) = 0, \quad (15)$$

with the potential  $v(r)$  in the matrix form

$$v(r) = \frac{1}{2} \begin{bmatrix} v(r) + v(-r), & v(r) - v(-r) \\ v(r) - v(-r), & v(r) + v(-r) \end{bmatrix} = \frac{1}{\sqrt{2}} \begin{bmatrix} v_0(r), & v_1(r) \\ v_1(r), & v_0(r) \end{bmatrix}. \quad (16)$$

The functions  $\psi(E, r)$  are routinely available in computations starting at near origin ( $r = 0$ ) with

$$[\psi(E, r)]_{l'l} = r^l \delta_{l'l}. \quad (17)$$

If in the asymptotic region, for  $r \geq S$ , these radial functions behave as

$$[\psi(E, r)]_{l'l} = j_{l'}(\sqrt{Er})[C(E)]_{l'l} - \frac{i}{\sqrt{E}}h_{l'}(\sqrt{Er})[S(E)]_{l'l} \quad (18)$$

then

$$[C(E)]_{l'l} = W \left\{ [\psi(E, r)]_{l'l}, -\frac{i}{\sqrt{E}}h_{l'}(\sqrt{Er}) \right\}_{r=S}, \quad (19)$$

$$[S(E)]_{l'l} = W \left\{ j_{l'}(\sqrt{Er}), [\psi(E, r)]_{l'l} \right\}_{r=S}, \quad (20)$$

with the Wronskian definition

$$W\{f, g\} = f \frac{\partial}{\partial r} g - g \frac{\partial}{\partial r} f. \quad (21)$$

Comparing (12) and (18) gives us the following relation for the  $t$ -matrix:

$$t(E) = S(E)C^{-1}(E). \quad (22)$$

The poles of the GF in (11) determine energy dispersion curves in the form of bands. These poles are usually found from zeros of the KKR-determinant

$$\det |t^{-1}(E) - B(E, k)| = 0. \quad (23)$$

Furthermore, we define the matrix of logarithmic derivatives

$$D(E, r) = \frac{\partial}{\partial r} [\psi(E, r)] [\psi(E, r)]^{-1}. \quad (24)$$

The  $D(E, r)$  matrix is not affected by changing of the regular solution normalization. Moreover, this matrix is symmetrical, i.e.

$$D^T(E, r) = D(E, r), \quad (25)$$

which can be proved by recalling that it satisfies the equation of Riccati type

$$\frac{\partial}{\partial r} D(E, r) + D^2(E, r) = v(r) - E \quad (26)$$

with the symmetrical potential matrix,  $v^T(r) = v(r)$ . At the ‘muffin-tin’ boundary point ( $r = S$ ), we can simply write

$$D(E) = \frac{\partial}{\partial r} [\psi(E, r)] \Big|_{r=S} [\psi(E, S)]^{-1}. \quad (27)$$

The log-derivative matrix  $D(E)$  is also directly related to the  $t$ -matrix by the following expression:

$$[v_P^{-1}(E)]_{l'l} = j_{l'}(\sqrt{ES})[t^{-1}(E)]_{l'l}j_{l'}(\sqrt{ES}) - \frac{i}{\sqrt{E}}h_{l'}(\sqrt{ES})j_{l'}(\sqrt{ES})\delta_{l'l} \quad (28)$$

with the definition of the pseudopotential amplitude matrix

$$v_P(E) = D(E) - D_0(E), \quad (29)$$

where

$$D_0(E) = \frac{d}{dr} [j(\sqrt{Er})] \Big|_{r=S} [j(\sqrt{ES})]^{-1}, \quad (30)$$

$$[j(\sqrt{Er})]_{l'l} = j_l(\sqrt{Er})\delta_{l'l}.$$

### 3. Novel forms of the KKR-matrix in one dimension

In the standard KKR-methodology, finding zeros of the matrix  $[t^{-1}(E) - B(E, k)]$  in the GF formula (11) is the central topic when computing energy bands. This is done by the requirement that at least one of the eigenvalues of that matrix goes through zero. In fact that condition comes out from analysing not the full GF in (11) but only from its second part. To circumvent this problem, we want the first term in equation (11) to vanish at the boundary radial points. This can be done by re-normalizing the regular solution as

$$\xi(E, r) = Z(E, r)Z^{-1}(E, S) \tag{31}$$

and accordingly the irregular solution

$$\zeta(E, r) = J(E, r)Z^T(E, S) - Z(E, r)j(\sqrt{E}S). \tag{32}$$

By direct calculations we may check that the Wronskian in matrix form defined as

$$W\{\zeta(E, r), \xi(E, r)\}_{r_l} = \left\{ \zeta^T(E, r) \frac{\partial}{\partial r} \xi(E, r) - \frac{\partial}{\partial r} \zeta^T(E, r) \xi(E, r) \right\}_{r_l} \tag{33}$$

is equal to

$$W\{\zeta(E, r), \xi(E, r)\} = W\{J(E, r), Z(E, r)\} = \mathbf{1}. \tag{34}$$

Setting in (31) and (32)  $r = S$  and recalling that  $t^T(E) = t(E)$ , it follows that

$$\xi(E, S) = \mathbf{1} \quad \zeta(E, S) = 0. \tag{35}$$

Now, we are in a position to convert the GF expressed in (11) using the convention  $(J, Z)$  to that in terms of  $(\zeta, \xi)$ . With the notation of the free GF matrix with radii on the ‘muffin-tin’ points as

$$[g_0(E, k)]_{r_l} = -\frac{i}{\sqrt{E}} h_l(\sqrt{E}S) j_l(\sqrt{E}S) \delta_{r_l} + j_r(\sqrt{E}S) [B(E, k)]_{r_l} j_l(\sqrt{E}S). \tag{36}$$

and with the use of equation (28), we get the following algebraic identity:

$$v_p^{-1}(E) - g_0(E, k) = J(E, S)[t^{-1}(E) - B(E, k)]J(E, S), \tag{37}$$

which can be converted into

$$[t^{-1}(E) - B(E, k)]^{-1} = J(E, S)[v_p^{-1}(E) - g_0(E, k)]^{-1}J(E, S). \tag{38}$$

The term on the left-hand side in equation (38) is also present in the master formula (11). We convert it further with the operator identity

$$[A - B]^{-1} = A^{-1} + A^{-1}[B^{-1} - A^{-1}]^{-1}A^{-1}, \tag{39}$$

applying it to the middle bracket on the right-hand side in (38) with the following result:

$$[t^{-1}(E) - B(E, k)]^{-1} = J(E, S)Z^{-1}(E, S) + Z^{-1}(E, S)[g_0^{-1}(E, k) - v_p(E)]^{-1}Z^{-1}(E, S). \tag{40}$$

When writing the first term on the right-hand side in equation (40) we made use of the algebraic identity

$$v_p^{-1}(E) = Z(E, S)J(E, S), \tag{41}$$

which can be proved by direct calculation using definitions (12) and (13). The expression in (40) is very convenient in passing from the convention  $(J, Z)$  to that in terms of  $(\zeta, \xi)$ , and

it can be directly inserted into (11) leading after extracting  $Z(E, S)$  and  $J(E, S)$  from (31) and (32) to the following new expression for the GF:

$$\langle x' | G(E, k) | x \rangle = \sum_{l_2 l_1} Y_{l_2}(\hat{x}') \langle l_2 r' | G(E, k) | l_1 r \rangle Y_{l_1}(\hat{x}) \quad (42)$$

with radial part

$$\begin{aligned} \langle l_2 r' | G(E, k) | l_1 r \rangle &= - \sum_l [\zeta(E, r_>)]_{l_2 l} [\xi(E, r_<)]_{l l_1}^T \\ &+ \sum_{l'l} [\xi(E, r')]_{l_2 l'} [g_0^{-1}(E, k) - v_P(E)]_{l'l}^{-1} [\xi(E, r)]_{l'l_1}^T. \end{aligned} \quad (43)$$

It follows from (43) that the GF with radial arguments at boundary points

$$[g(E, k)]_{l_2 l_1} \equiv \langle l_2 S | G(E, k) | l_1 S \rangle \quad (44)$$

can be found from the algebraic equation of Dyson type

$$g(E, k) = g_0(E, k) + g_0(E, k) v_P(E) g(E, k) \quad (45)$$

with pseudopotential amplitude  $v_P(E)$  as given in (29). The poles of  $g(E, k)$  are exactly the same as of the full GF  $\langle x' | G(E, k) | x \rangle$  in (11), suggesting an alternative way to (23) of finding the energy bands

$$\det |g^{-1}(E, k)| = 0. \quad (46)$$

Searching for zeros of the eigenvalues of the matrix  $g^{-1}(E, k)$  is much easier than that of  $t^{-1}(E) - B(E, k)$  as the eigenvalue functions of the former are monotonically increasing with energy  $E$ . But some obscuring deficiency still persists, as the slopes at which these eigenvalues are crossing the energy axis are not fixed. This inconvenience can be avoided in the following way. Let us first integrate the GF in the form (43) over the whole Wigner–Seitz (WS) cell:

$$\begin{aligned} \int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle &= - \sum_l \int_{-a/2}^{a/2} dx \zeta_l(E, x) \xi_l(E, x) \\ &+ \sum_{l'l} [g(E, k)]_{l'l} \int_{-a/2}^{a/2} dx \xi_{l'}(E, x) \xi_l(E, x). \end{aligned} \quad (47)$$

Integrating the first term in (47) yields

$$\begin{aligned} \int_{-a/2}^{a/2} dx \zeta_l(E, x) \xi_l(E, x) &= \sum_{l_2 l_1} \int_0^S dr \sum_{\hat{x}} Y_{l_2}(\hat{x}) Y_{l_1}(\hat{x}) [\zeta(E, r)]_{l_2 l'} [\xi(E, r)]_{l'l_1} \\ &= \int_0^S dr [\zeta^T(E, r) \xi(E, r)]_{l'l}. \end{aligned} \quad (48)$$

From the Schrödinger equation we find that the radial parts  $\zeta^T(E, r)$  and the energy derivative  $\frac{\partial}{\partial E} \xi(E, r) \equiv \dot{\xi}(E, r)$  satisfy the differential equations

$$\frac{d^2}{dr^2} \zeta^T(E, r) = \zeta^T(E, r) [v(r) - E] \quad (49)$$

and

$$\frac{\partial^2}{\partial r^2} \dot{\xi}(E, r) = [v(r) - E] \dot{\xi}(E, r) - \xi(E, r) \quad (50)$$

respectively. Multiplying (49) to the right by  $\xi(E, r)$ , then (50) to the left by  $\zeta^T(E, r)$  and subtracting one from the other, we get

$$\int_0^S dr \zeta^T(E, r) \xi(E, r) = W \{ \zeta(E, r), \dot{\xi}(E, r) \}_{r=0}. \quad (51)$$

This integral can be conventionally found if the function  $\psi(E, r)$  (17) is computed. From the definition of  $\xi(E, r)$  in (31) it follows that

$$\xi(E, r)\psi(E, S) = \psi(E, r), \tag{52}$$

$$\dot{\xi}(E, r)\psi(E, S) + \xi(E, r)\dot{\psi}(E, S) = \dot{\psi}(E, r) = 0 \quad (r \rightarrow 0). \tag{53}$$

Inserting  $\dot{\xi}(E, r)$  from (53) into (51) we get

$$\begin{aligned} W\{\zeta(E, r), \dot{\xi}(E, r)\}_{r=0} &= W\{\zeta(E, r), -\xi(E, r)\dot{\psi}(E, S)\psi^{-1}(E, S)\}_{r=0} \\ &= -\dot{\psi}(E, S)\psi^{-1}(E, S). \end{aligned} \tag{54}$$

Combining (51) with the result (54) we have

$$\int_0^S dr \zeta^T(E, r)\xi(E, r) = -\dot{\psi}(E, S)\psi^{-1}(E, S). \tag{55}$$

For the second integral in (47) we obtain

$$\begin{aligned} \int_{-a/2}^{a/2} dx \xi_{l'}(E, x)\xi_l(E, x) &= \int_0^S dr [\xi^T(E, r)\xi(E, r)]_{l'l} \\ &= [N_\psi(E)\psi^{-1}(E, S)]^T [N_\psi(E)\psi^{-1}(E, S)] \end{aligned} \tag{56}$$

with the definition of  $N_\psi(E)$  as

$$\int_0^S dr \psi^T(E, r)\psi(E, r) = N_\psi^T(E)N_\psi(E). \tag{57}$$

With the help of (55) and (56) we may convert (47) to the form

$$\begin{aligned} \int_{-a/2}^{a/2} \langle x | G(E, k) | x \rangle &= \sum_l [\dot{\psi}(E, S)\psi^{-1}(E, S)]_{l'l} \\ &+ \sum_l \{ [N_\psi(E)\psi^{-1}(E, S)] g(E, k) [N_\psi(E)\psi^{-1}(E, S)]^T \}_{ll} \\ &= \sum_l P_{ll}(E, k). \end{aligned} \tag{58}$$

The left-hand side of equation (58) is equal to the trace of the Hermitian matrix  $P(E, k)$  defined as

$$P(E, k) = 1/2[Q(E, k) + Q^\dagger(E, k)], \tag{59}$$

with

$$\begin{aligned} Q(E, k) &= [\psi(E, S)N_\psi^{-1}(E)]^{-1}[\dot{\psi}(E, S)N_\psi^{-1}(E)] \\ &+ N_\psi(E)\psi^{-1}(E, S)g(E, k)[N_\psi(E)\psi^{-1}(E, S)]^T. \end{aligned} \tag{60}$$

The poles of the matrix  $P(E, k)$  give energy bands that can be found from zeros of the determinant

$$\det |P^{-1}(E, k)| = 0. \tag{61}$$

From the analytical structure of the GF known in the literature as the Herglotz property explicitly given in [10], it is expected that

$$\frac{\partial}{\partial E} \lambda_i [P^{-1}(E, k)] > 0. \tag{62}$$

Any failure to this condition may result in an unphysical negative contribution to the density of states. The formal proof can be traced back as a consequence of the GF property used in



deriving the Lloyd formula and given in (78), which also supports the expectation that the slope at which the eigenvalue curves cross the energy axis is equal to one.

In formula (60) the presence of the inverse matrix  $\psi^{-1}(E, S)$  may cause numerical instability if matrix  $\psi(E, S)$  is singular, which may happen in practice. To avoid such complications it is convenient to combine the first and second terms in equation (59) with the following manipulation. First, we can compute the integral in (57) using a trick with the energy derivative, like in (49) and (50). Then with the known procedure we get

$$\int_0^S dr \psi^T(E, r)\psi(E, r) = -W\{\psi(E, r), \dot{\psi}(E, r)\}_{r=S}. \quad (63)$$

In equation (63) the contribution at the origin point ( $r = 0$ ) is set to be equal to zero, which is justified with the normalization of  $\psi(E, r)$  assumed in equation (17). Recalling the Wronskian definition, as set in (21), and log-derivatives in (27), we may proceed with (63) getting

$$\int_0^S dr \psi^T(E, r)\psi(E, r) = \psi^T(E, S)\{D_\psi(E) - D_{\dot{\psi}}(E)\}\dot{\psi}(E, S). \quad (64)$$

From (64) and (57) there follows the equality

$$[\psi(E, S)N_\psi^{-1}(E)]^T\{D_\psi(E) - D_{\dot{\psi}}(E)\}[\dot{\psi}(E, S)N_\psi^{-1}(E)] = 1, \quad (65)$$

which is useful in converting (60) to the desired form as follows:

$$Q(E, k) = [\psi(E, S)N_\psi^{-1}(E)]^{-1}\{\dot{\psi}(E, S)N_\psi^{-1}(E) + g(E, k)[\psi(E, S)N_\psi^{-1}(E)]^{-1T}\}. \quad (66)$$

From (66) with the help of equality (65) we may proceed to

$$Q(E, k) = [\psi(E, S)N_\psi^{-1}(E)]^{-1}\{[D_\psi(E) - D_{\dot{\psi}}(E)]^{-1} + g(E, k)\}[\psi(E, S)N_\psi^{-1}(E)]^{-1T}. \quad (67)$$

But recalling  $g(E, k)$  as given in (45) we get

$$\begin{aligned} & [D_\psi(E) - D_{\dot{\psi}}(E)]^{-1} + g(E, k) \\ &= [g_0^{-1}(E, k) + D_0(E) - D_\psi(E)]^{-1}[g_0^{-1}(E, k) + D_0(E) - D_{\dot{\psi}}(E)] \\ & \quad \times [D_\psi(E) - D_{\dot{\psi}}(E)]^{-1}, \end{aligned} \quad (68)$$

which if inserted in (67) gives

$$\begin{aligned} Q(E, k) &= \{\psi(E, S)N_\psi^{-1}(E) + g_0(E, k)[D_0(E) - D_\psi(E)]\psi(E, S)N_\psi^{-1}(E)\}^{-1} \\ & \quad \times \{\dot{\psi}(E, S)N_\psi^{-1}(E) + g_0(E, k)[D_0(E) - D_{\dot{\psi}}(E)]\dot{\psi}(E, S)N_\psi^{-1}(E)\}. \end{aligned} \quad (69)$$

With the Wronskian definition as in (21) this last expression can be simplified further:

$$\begin{aligned} Q(E, k) &= N_\psi(E) \left\{ \psi(E, S) + C(E, k)W^T[\psi, j] \right\}^{-1} \\ & \quad \times \left\{ \dot{\psi}(E, S) + C(E, k)W^T[\dot{\psi}, j] \right\} N_\psi^{-1}(E) \end{aligned} \quad (70)$$

with the matrix  $C(E, k)$  formed from KKR structure functions  $B(E, k)$ :

$$[C(E, k)]_{rl} = -\frac{i}{\sqrt{E}}h_{rl}(\sqrt{E}S)\delta_{rl} + j_{rl}(\sqrt{E}S)[B(E, k)]_{rl}. \quad (71)$$

These two last equations give the most convenient way to construct the novel KKR-matrix  $P(E, k)$  with desired properties of the eigenvalues.

#### 4. Generalized Lloyd formula

The Lloyd formula [6] is often used to calculate the number of states for a ‘muffin-tin’ model potential [5]. We derive it here in the form similar to that used in the paper by Kaprzyk and Bansil [7].

It is well known that the total number of states per unit cell  $N(E)$  is written as

$$N(E) = -\frac{1}{\pi} \text{Im} \int_{-\infty}^E dE \frac{1}{N_u} \sum_{k \in \text{BZ}} \int_{(WS)} dx \langle x | G(E, k) | x \rangle \quad (72)$$

where  $N_u$  is the number of unit cells in the crystal. We show that the space integral in (72) can be expressed as a perfect energy derivative and that the energy integration can be done explicitly. We start with (58), putting it in the form

$$\begin{aligned} \int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle &= \text{Tr} \{ \psi^{-1}(E, S) \dot{\psi}(E, S) \} \\ &+ \text{Tr} \{ g(E, k) [N_\psi(E) \psi^{-1}(E, S)]^T [N_\psi(E) \psi^{-1}(E, S)] \}. \end{aligned} \quad (73)$$

Then with the help of (64) we find (at  $r = S$ )

$$N_\psi^T(E) N_\psi(E) = -\psi^T(E, S) \dot{D}_\psi(E) \psi(E, S). \quad (74)$$

With the last result, (73) can be written as

$$\int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle = \text{Tr} \{ \psi^{-1}(E, S) \dot{\psi}(E, S) \} - \text{Tr} \{ g(E, k) \dot{D}_\psi(E) \}. \quad (75)$$

The last step consists of proving the equality

$$\frac{\partial}{\partial E} g(E, k) = g(E, k) \dot{D}_\psi(E) g(E, k), \quad (76)$$

which if inserted into (75) gives the result

$$\int_{-a/2}^{a/2} dx \langle x | G(E, k) | x \rangle = -\frac{\partial}{\partial E} \text{Tr} \ln [g(E, k) \psi^{-1}(E, S)]. \quad (77)$$

The algebraic equality (76) is a consequence of GF properties stating that

$$\frac{\partial}{\partial E} G(E) = -G(E) G(E). \quad (78)$$

If applied to our Bloch–Fourier GF with radial arguments on ‘muffin-tin’ boundary points, we get

$$\langle \hat{x}_2 S | \frac{\partial}{\partial E} G(E, k) | \hat{x}_1 S \rangle = - \int_{-a/2}^{a/2} dx \langle \hat{x}_2 S | G(E, k) | x \rangle \langle x | G(E, k) | \hat{x}_1 S \rangle \quad (79)$$

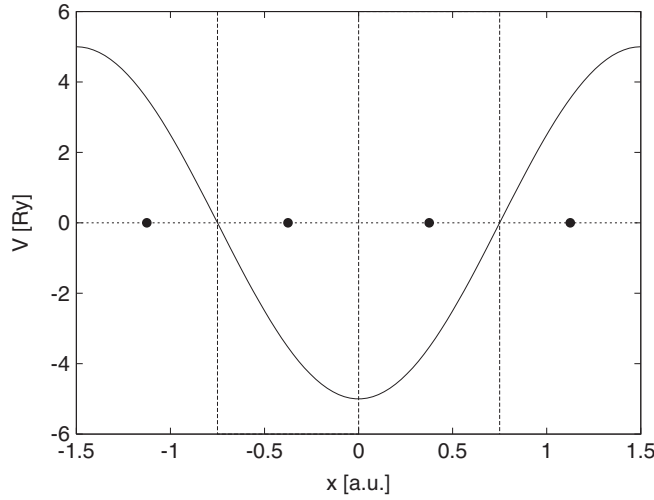
and for the radial part defined in (42)

$$\langle l_2 S | \frac{\partial}{\partial E} G(E, k) | l_1 S \rangle = - \int_0^S dr \langle l_2 S | G(E, k) | lr \rangle \langle lr | G(E, k) | l_1 S \rangle. \quad (80)$$

Here the integral on the right-hand side in (79) is only over the WS cell because we deal with the Bloch–Fourier GF which is periodic and its arguments are defined only inside one cell. Inserting proper radial arguments into (43) we get according to (35) and (44) that

$$\langle l_2 S | G(E, k) | lr \rangle = [g(E, k) \xi^T(E, r)]_{l_2 l}, \quad (81)$$

$$\langle lr | G(E, k) | l_1 S \rangle = [\xi(E, r) g(E, k)]_{ll_1}, \quad (82)$$



**Figure 1.** The Mathieu potential used in the calculations. The black dots denote four atoms in the unit cell case. In the case of one atom, it is placed in the middle of the unit cell.

which allows us to rewrite (80) in the form

$$\frac{\partial}{\partial E}[g(E, k)] = -g(E, k) \left[ \int_0^S dr \xi^T(E, r) \xi(E, r) \right] g(E, k). \quad (83)$$

Computing the integral in (83) can be done with the help of (74), and leads to the result

$$\int_0^S dr \xi^T(E, r) \xi(E, r) = -\dot{D}_\xi(E) = -\dot{D}_\psi(E). \quad (84)$$

Inserting this relation into (83) proves the validity of (76). The total number of states per unit cell seen in (72) can now be found from

$$N(E) = \frac{1}{\pi} \text{Im} \ln(\det |\psi(E, S)|) - \frac{1}{\pi} \frac{1}{N_u} \sum_{k \in \text{BZ}} \text{Im} \ln \det |g(E, k)|. \quad (85)$$

In passing from (77) to (85) we used the algebraic equality

$$\text{Tr} \ln[A] = \ln[\det |A|]. \quad (86)$$

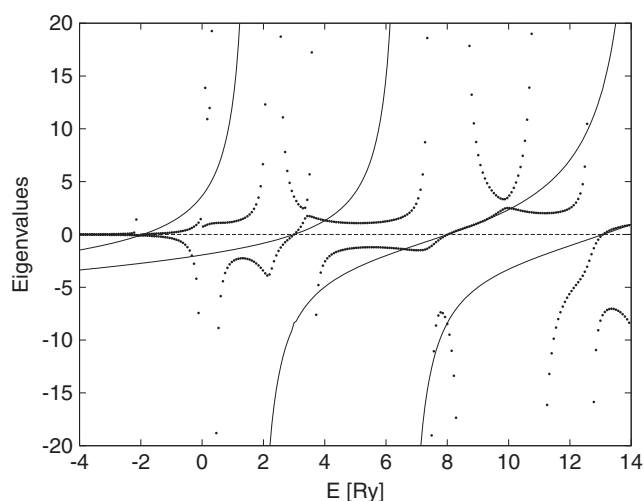
In (85) the first term accounts for the number of nodes on the regular solution from the origin up to radius  $S$ , and the second term comes from the Bloch states at each of the  $N_u$   $k$ -points in BZ.

## 5. Results

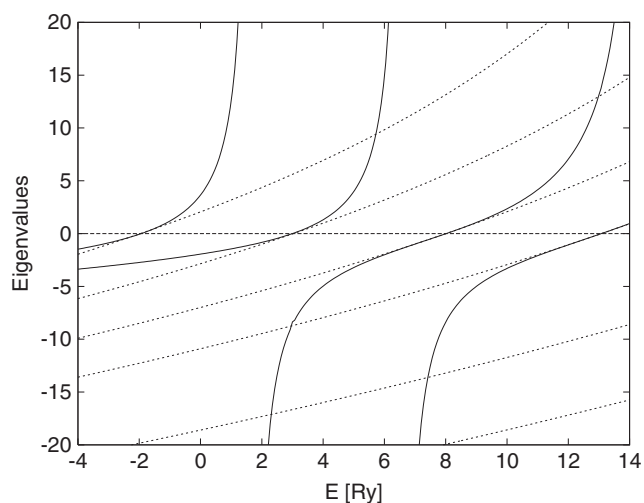
In order to illustrate numerically how the novel approach to the KKR method works compared to the standard one, we have performed calculations for the 1D Mathieu potential of the form

$$v(x) = -U_0 \cos(2\pi x/a), \quad (87)$$

and used the lattice constant  $a = 3.0$  au and  $U_0 = 5$  Ryd (see figure 1). In figure 2 we show the eigenvalue functions as calculated using both the standard and novel methods (equations (23) and (61)) for the potential (87). One can see that the zeros of the eigenvalue functions are exactly the same. In the novel method case we can find them numerically very easily, but in the



**Figure 2.** Comparison of the standard KKR method (dots) and the novel one (solid curves) as applied to the Mathieu potential (87). The wavevector is  $k = 0.6\pi/a$ .



**Figure 3.** The eigenvalue functions for the Mathieu potential (87) and the wavevector  $k = 0.6\pi/a$ . The cases with one and four atoms in the unit cell are represented by solid and dashed curves, respectively.

standard KKR approach it is much more difficult. Moreover, to illustrate how the eigenvalue curves behave when the number of atoms in the unit cell grows, we performed the calculations in two cases. In the first case we put only one atom in the unit cell with the ‘muffin-tin’ radius  $S = 1.5$  au and the symmetric potential given by (87). In the second case we divided the unit cell into four ‘muffin-tin’ segments of the same length and touching each other, but without changing the total potential in the unit cell. So, in this case the potential in each segment is not symmetrical, but the physical situation is exactly the same. What changed is the size of the resulting matrices and hence the number of the eigenvalue functions. These functions in both cases are shown in figure 3 for the wavevector  $k = 0.6\pi/a$ . Note that in the second case

the lines are not derived from interpolation but simply connect calculated points, which are not shown in figure 3.

Now all the benefits of the novel method can be underlined. First, we observe that the eigenvalue functions do not cross each other and grow monotonically. Moreover, they form almost straight lines with a slope of unity when passing through zero. Secondly, we can see that with the increasing number of atoms in the unit cell the eigenvalue curves become straight for the wider range of energies. So, in the limit of an infinite number of atoms in the unit cell, the method seems to become linear. This makes the method not very sensitive to the number of energy points used in the interpolation procedure, when finding zeros of eigenvalue curves. This last advantage opens possibilities for the calculation of very complex systems, even with hundreds of atoms in the unit cell, in reasonable time without losing accuracy.

## 6. Summary

In this paper we have reformulated the one-dimensional full potential KKR formalism. Then we have derived a novel form of the KKR secular matrix. To exclude the first term in the full Green function we have normalized solutions of the Schrödinger equation in such a way that the ‘irregular’ solution disappears at the boundary points of ‘muffin-tin’ segments. Then by integrating the full Green function over the Wigner–Seitz cell we have derived the final result, that is the expressions for the secular matrix  $P(E, k)$  as well as for the generalized Lloyd formula. The eigenvalues of the inverse matrix  $P^{-1}(E, k)$  increase monotonically with energy and almost linearly for every  $k$ -point. In the case of increasing number of atoms in the unit cell the eigenvalue functions become more linear.

Finally, we performed numerical calculations for the case of the Mathieu potential. The results show that the zeros of the eigenvalues can be easily found, even for very complex systems, without any loss of accuracy. This formalism can be extended to higher-dimensional systems with minor changes.

## Appendix

In this appendix we briefly generalize the formalism introduced in sections 2–4 for many atoms in the unit cell. In this case one has to solve the Schrödinger equation with the potential

$$V(x) = \sum_{n=-\infty}^{\infty} \sum_{\alpha=1}^p v_{\alpha}(x - na - a_{\alpha}), \quad (\text{A.1})$$

where  $a_{\alpha}$  is the position of the  $\alpha$ th atom in the unit cell with  $p$  equal to the number of atoms in the unit cell. At each ‘muffin-tin’ atomic segment we solve the Schrödinger equation starting at the origin from

$$[\psi^{\alpha}(E, r)]_{l'l} = r^l \delta_{l'l} \quad r \rightarrow 0. \quad (\text{A.2})$$

The resulting  $\psi$  matrix has the form

$$[\psi(E, r)]_{\alpha'l', \alpha l} = [\psi^{\alpha}(E, r)]_{l'l} \delta_{\alpha'l \alpha} \quad (\text{A.3})$$

with size  $2p \times 2p$ . Similarly we construct all other matrices introduced in the previous sections. The GF in  $(\zeta, \xi)$  representation now has a form

$$\begin{aligned} \langle x' + a_{\alpha'} | G(E, k) | x + a_{\alpha} \rangle = & - \sum_l \xi_l^{\alpha'}(E, x_{>}) \xi_l^{\alpha}(E, x_{<}) \delta_{\alpha\alpha'} \\ & + \sum_{l, l'} \xi_{l'}^{\alpha'}(E, x') [g_0^{-1}(E, k) - v_P(E)]_{\alpha'l', \alpha l}^{-1} \xi_l^{\alpha}(E, x). \end{aligned} \quad (\text{A.4})$$

The structure constants in this generalized case can be given explicitly with the matrix elements  $[B(E, k)]_{\alpha'\alpha}$ :

$$[B(E, k)]_{\alpha 0, \alpha' 0} = [B(E, k)]_{\alpha 1, \alpha' 1} = \frac{\exp(i\sqrt{E}a) \cos \sqrt{E}a_{\alpha\alpha'} - \cos(ka - \sqrt{E}a_{\alpha\alpha'})}{i\sqrt{E}[\cos ka - \cos \sqrt{E}a]} + \frac{1}{i\sqrt{E}} \exp(i\sqrt{E}|a_{\alpha\alpha'}|)(1 - \delta_{\alpha\alpha'}), \quad (\text{A.5})$$

$$[B(E, k)]_{\alpha 1, \alpha' 0} = [B(E, k)]_{\alpha' 0, \alpha 1}^* = -\frac{\exp(i\sqrt{E}a) \sin \sqrt{E}a_{\alpha\alpha'} + \sin(ka - \sqrt{E}a_{\alpha\alpha'})}{i\sqrt{E}[\cos ka - \cos \sqrt{E}a]} - \frac{1}{\sqrt{E}} \exp(i\sqrt{E}|a_{\alpha\alpha'}|) \operatorname{sgn}(-a_{\alpha\alpha'}), \quad (\text{A.6})$$

with  $a_{\alpha\alpha'} = a_{\alpha} - a_{\alpha'}$ . Finally we define the matrix  $P(E, k)$  by the relation

$$\sum_{\alpha} \int_{-S_{\alpha}}^{S_{\alpha}} dx \langle x + a_{\alpha} | G(E, k) | x + a_{\alpha} \rangle = \operatorname{Tr}[P(E, k)], \quad (\text{A.7})$$

with  $S_{\alpha}$  being the muffin-tin radius of the  $\alpha$ th atom. Following the steps described in previous sections we find that the matrix  $P(E, k)$  can be found using equations (59) and (60) by adding atomic indices to the matrix elements, as is done for the structure constants matrix  $B(E, k)$ . The band structure is still determined by relation (61).

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